AN OCCUPATIONAL SYNDROME AMONG WORKERS IN ZINC*

CAREY P. McCORD, M.D., Fellow A.P.H.A., and
ALFRED FRIEDLANDER, M.D.

Industrial Health Conservancy Laboratories; and University of Cincinnati, Cincinnati, O.

IN THE galvanizing room of a sheet metal plant under our medical supervision, the incidence of gastrointestinal diseases during the past 3 years has been exceptionally high. In the early part of 1925, the demonstration of gastric ulcers in one of these workers led to an inquiry as to the nature and cause of this condition among these galvanizers.

Of the 20 men engaged in this work, 15 had been employed over a long period of years (6 to 22). Twelve of these 15 exhibited characteristics of severe gastrointestinal inflammation culminating, in a few instances, in well established gastric or duodenal ulcers.

The outstanding features of the series of 12 cases are:

A. Marked anemia, pallor
B. Gastrointestinal manifestations of a character commonly associated with ulcer or pre-ulcer conditions
C. Constipation—abdominal distress more marked when constipated
D. Persistent headache

Although not more than 20 men have been employed at any one time, a larger number of workers have been observed, owing to the labor turnover. In no worker whose employment period has been less than 5 years has there been any complaint approximating the severity described above. A few have complained of fleeting gastritis, hyperacidity, etc. The men of the group under observation as a rule have been drinkers, of low intelligence, excessive users of tobacco, having bad eating habits, and the majority presented bad mouth conditions. Economic conditions have also caused worries and stress. With few exceptions, all of these workers are related either by blood or marriage. Many have failed to coöperate with us and it has been impossible to carry out valuable diagnostic tests; gastric analyses have been out of the question. In some instances X-ray examination, urinalyses or blood counts have been unobtainable.

This low type of worker is found in other departments in this plant, and in other plants under our observation. Among the 200 other workers in the plant only 1 case of gastric ulcer has been detected in the course of the 3 years of our work. In view of the high incidence limited to this small group of galvanizers, and in view of the appearance of the disease only among long time workers, we suspected the work processes of being the possible causative agent.

TRADE PROCESSES INVOLVED IN GALVANIZING

In the quest for the cause of this occupational disease, investigations were carried out in two plants. In plant 1 these cases have been detected. In plant 2 no cases of this occupational disease have been found, but acute zinc poisoning is known to have occurred. In plant 2 no workers except foremen have been engaged for as long a period as 6 years.

"Galvanizing" is the term designating the coating of iron or steel with zinc.

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The first step is to prepare the material to be galvanized so as to present a clean metal surface, in order that it can " take " the coat of zinc. The cleansing with acids of iron from adhering rust, scale, or other foreign substances is known as " pickling." There are several acids that may be used—sulphuric, hydrochloric, and hydrofluoric acids. Sulphuric acid is the agent most commonly employed.

In Plant 1 the various tubs, buckets, cans, etc., to be galvanized are made from sheet iron. These sheet metal objects are placed in a large vat containing water and sulphuric acid. A gross rule of thumb governs the concentration and temperature to be maintained. A solution of 7.5 per cent acid and a temperature of 150° F. probably represents optimum conditions. The sulphuric acid in this weak solution is not freely volatile, but steam arising from the vat readily carries the sulphuric acid. Also, into this pickling bath is placed an unmeasured quantity of a preparation having the trade name of " Klean-rite." An analysis of this proves it to be 98 per cent sodium chloride and 2 per cent organic material. In the pickling process large volumes of hydrogen are evolved. White [1] points out that as much as 1.05 c.c. of hydrogen may be set free from every square inch of iron metal following pickling. This liberated hydrogen is capable of combining with the sulphur present as an impurity, and with the arsenic found as an impurity in zinc.

Some sulphuric acid used in pickling is reported as containing admixed nitric acid. In a few galvanizing plants such chemicals are added as will lead to the production of hydrofluoric acid. We believe that neither of these hazards need be contemplated in this investigation. After pickling, the sheet iron objects are sometimes immediately submerged in molten zinc, but at other times are rinsed in dilute hydrochloric acid solution at room temperature. Some galvanizing plants allow for drying before submerging in molten zinc; others rinse in plain water, but in Plant 1 the object is submerged wet from the dilute acid.

The zinc chamber is roughly 4′ x 8′ x 3′ in depth. Heating is obtained through the use of city gas, which is known to contain a small percentage of carbon monoxide. A flue for oven fumes extends above the level of the workers' heads, emptying into a larger hood placed over the entire zinc chamber. The molten zinc is kept at a temperature of 468° C. The surface of the molten zinc is divided into two parts by a partition. Upon the surface of one part there is superimposed a layer of salammoniac that serves as a flux. In addition to ammonium chloride used in this step, admixed zinc chloride is often used. Mixed with the salammoniac are small quantities of " cereal middlings " to fluff it up. From time to time during the day, there is placed into the molten zinc small bars of a commercial combination of metals called " silver metal." This serves as a brightener for the galvanized surface. This contains aluminum, antimony and tin. Several workers stand directly over the molten zinc. These workers are engaged in submerging and lifting out articles to be galvanized. The work is at a high temperature at all seasons. The galvanized articles are allowed to drip free of molten metal and after a very few minutes are removed for stripping of adhering particles and for storage.

The foregoing processes for galvanizing hold true in a general way for all plants galvanizing small articles—cans, tubs, and such utensils.

In Plant 2, the galvanizing is limited to flat sheets of metal. All sheets are of the same size and essentially all processes are carried out by machinery. Instead of recounting in detail the trade processes involved, only those items will be mentioned which differ from those described above. In the latter plant, after pickling by machine dipping, all sheet metal is redipped in lime water to neutralize the effects of the acid. Although vapors arise visibly from both of these kinds of vats, there is no obvious mingling of fumes until they are far above the breathing level of workers. These vats are some distance away from the molten zinc vat where again no intermingling of fumes is noticeable at low levels. Prior to submersion in molten zinc a dipping is made into ordinary water. It is believable, therefore, that no gross formation of zinc chloride or zinc sulphate takes place at this point. Other differences of lesser import have been noted, such as the use of tallow as the fluffing agent instead of middlings, and the blowing of sulphur dioxide fumes over the surface of the molten zinc.

PLANT 1	PLANT 2
1. The workroom is small, with low (12 ft.) ceiling and visible mingling of fumes.	1. The workroom is very large with the ceiling 65 feet above ground level, with mingling of fumes only at high levels.
2. The pickling and galvanizing vats are placed relatively close together, favoring the admixture of fumes.	2. Vats for pickling and galvanizing are at a greater distance.
3. All work is done by hand with men in close proximity to chemicals employed.	3. All work is done by machinery with men kept at considerable distance.
4. Pickled objects, wet with acid, are submerged directly in molten zinc through flux of salammoniac.	4. Pickled objects are submerged in lime water to neutralize the acid, and later into tap water prior to submerging in molten zinc through flux of salammoniac.
5. Majority of workers employed in excess of 6 years.	5. Practically all workers employed less than 6 years.
6. " Silver metal " used.	6. " Silver metal " not used.

It has already been noted that in Plant 2 no cases of the occupational disease under study have arisen. It is believable from analyses made that the same impurities of crude materials are common to each plant. The type of workmen is similar although no old timers are found in Plant 2, owing to past labor difficulties. The above differences in the processes involved may serve to explain the difference in health conditions.

ANALYSES OF MATERIALS AND DUSTS *

Since in our opinion exposure over long periods of time is necessary to develop the condition being studied, not a great deal of information is to be gained from analyses of materials used at this immediate time. Materials in use in the course of 20 years have been obtained from different sources, made by different processes, without doubt containing varying quantities of impurities. Analyses have been made on some materials; in other instances acceptable recorded analyses have been utilized. It is our purpose in recording these analyses to indicate the general character of impurities contained therein.

The sheet iron, later to be galvanized, presented the following impurities: carbon, manganese, sulphur and phosphorus. The quantity of these impurities varies. According to White [1] the percentage is approximately: carbon, .13 per cent; manganese, .38 per cent; sulphur, .045 per cent; phosphorus, .065.

The salammoniac tested 98 per cent ammonium chloride.

Analyses of spelter, by Ingalls,[2] are accepted by us as representing the average spelter in use. One analysis is here cited, showing the impurities mixed in with the zinc.

Pb%	Fe%	Cd%	As%	Sb%
0.0701	0.7173	......	0.0603	0.0249
Cu%	Bi%	SiO%	S%	C%
0.1123	......	0.0346	0.0035	0.1775

The sulphuric acid in current use tested 76.9 per cent. Traces of lead were found and negligible traces of unrelated impurities were detected.

*A portion of the analytical investigation was conducted by The Langdon-Meyer Laboratories, Cincinnati, Ohio.

Analyses of dust settlings taken from ledges near the galvanizing vat in Plant 1 were made on several occasions, of which two are cited:

PLANT 1

Qualitative Analysis

A sample of the dust settling above the galvanizing pot and representing probably the condensable portion of the fumes to which the operator is subject, shows a trace of antimony, much zinc, iron, sulphides, sulphates, chlorides, as well as some material insoluble in strong boiling acids.

Quantitative Analysis

Sulphur as sulphates (SO_3)	14.20%
Iron and aluminum oxids	8.92%
Zinc as Zn	35.00%
Ammonia as NH_4	6.25%
Chlorides, Cl_2	18.50%
Sulphur as sulphide	.08%
Silica, SiO_2	1.05%
Calcium	Traces
Arsenic	Doubtful traces

In Plant 2, a specimen of ledge dust was taken at a level of about 45 feet above the heads of the workers. An analysis exhibits constituents as follows:

PLANT 2

Quantitative Analysis

Sulphur as sulphates (SO_3)	17.29%
Iron and aluminum oxides	6.65%
Zinc as Zn	45.6 %
Ammonia as NH_4	10.35%
Chlorides as Cl_2	13.36%
Hydrogen sulphide	.06%
Lead	Traces
Tin	Traces
Water soluble material	55.32%
Antimony	0
Arsenic	0

A qualitative analysis of "spelter dross" revealed zinc, iron and aluminum, together with doubtful traces of arsenic.

In the galvanizing room of Plant 1, zinc oxide comes into contact with sulphuric acid in the presence of moisture. The combination of these two substances leading to the formation of zinc sulphate is regarded by us as a certainty. Similarly, the combination of zinc with hydrochloric acid leads to the formation of zinc chloride. One of the consulting chemists aiding us on this point sought to determine the precise amount of these zinc salts through methods based on measurement of total amount of molecular material available for combination. The figures indicate the presence of zinc sulphate in the ledge dusts of Plant 1 to the extent of 15 per cent, and zinc sulphide to the extent of .72 per cent. Other chemists accept with certainty the presence of zinc sulphate, zinc chloride and zinc sulphide, but recommend the avoidance of fixing any precise percentage.

In Plant 2 another possible source of zinc sulphate is in the combination of the zinc with the products of burned sulphur when the latter is used as a displacer of air from the machine rollers. An additional source of zinc chloride is found when salammoniac is used on the surface of the zinc vat. Thorpe [3] attests to the formation of zinc chloride under the conditions mentioned.

From these various analyses, recognition must be given to a number of potentially harmful substances, such as: hydrogen sulphide, arseniureted hydrogen, arsenic, mineral acids, ammonia, ammonium chloride, lead, antimony, cadmium, aluminum, tin and zinc.

We are disposed to regard the salts of zinc, accidentally formed under the conditions just described, as possible causative factors in bringing about the lesions of our cases. We are influenced in this concept by the results obtained in experimental work following the administration of pure metallic zinc and zinc salts. In galvanizing, the zinc hazard has heretofore largely been attributed to zinc oxide, which substance is known to bring about acute zinc poisoning characterized by chills. In order to produce zinc chills, the zinc oxide must have been recently burned and, according to Drinker,[4] the zinc oxide must be in the physico-chemical state of dispersion rather than the state of flocculation. Reference is made to Drinker's excellent paper for a critical review of the literature of zinc oxide toxicology. We have no reason to believe that there is any relation between acute zinc poisoning and the chronic condition described by us. Any toxic properties of zinc resulting in chronic industrial disease has heretofore been largely denied. It is generally admitted, however, that workers in zinc often present chronic industrial diseases. These conditions are usually blamed on antimony, arsenic, or lead, which are found in these processes as impurities either in the zinc or in the substances used in conjunction with zinc, such as sulphuric acid. The characteristics of these occupational diseases (lead, arsenic and antimony) are fairly well known. However, upon close examination of workers in zinc the manifestations of their diseases do not convincingly coincide with these known characteristics.

THE GENERAL TOXICOLOGY OF ZINC

Zinc may be found in various human tissues and excreta as a result of eating foods containing zinc. Shellfish are known to normally contain zinc, according to Bodansky.[5] Van Itallie,[6] in discussing the normal content of zinc, arsenic, and copper in the human body reports the finding of appreciable quantities in the liver of 24 subjects. Ghiglotto [7] examined the organs of 22 persons dead of accidents. The zinc content (as Zno) varied from .0015 to .0028 per cent of the viscera. Zinc was also found in the fetus.

Rost [8] has found among non-industrial workers the presence of zinc in urine and feces. The average daily excretion in the urine ranges from .6 to 1.6 mg. (as zinc oxide), and in the feces varied from 9 mg. to as high as 39 mg. The source of the zinc is to be found in galvanized pipes, cooking vessels, cosmetics, etc. Salkowski [9] tested plum marmalade made in a zinc-lined vessel and a zinc content of 3.4 per cent was found, estimated as the sulphate. Peterson, Haines and Webster [10] point out that milk, vinegar, soup, olive oil, etc., may be contaminated with zinc from storage in zinc containers. Some zinc is found in practically all foods. The zinc content in samples of beef, veal, pork, and mutton ranged from 26 to 50 mg. per kg.; in beef liver a maximum of 83 mg. per kg. was found; in bread from 5 to 8 mg.; in dried vegetables 6.13 mg. and in cow's milk 3.9 mg.[8] Giaya [11] examined 8 human subjects ranging from the unborn to 70 years. In all of these, zinc was found. The amount increased in proportion to the age. His findings convinced him that zinc toxicity is lacking when stored zinc is less than .05 g. per kg. of viscera. From the foregoing, it is obvious that the qualitative detection of zinc in human organs or excreta may be without significance. In man the zinc content in mg. per kg. of tissue was found by Rost [8] to be: liver, 52 to 146; musculature, 47 to 52; brain, 11. Zinc workers excrete zinc long after they discontinue work in zinc industries. Rost believes that zinc may be absorbed through the intestinal tract, stored in the liver and muscles, excreted in the urine, feces and milk. Salant, Rieger and Treuthardt [12] find that zinc is stored in considerable quantities in the liver.

These data establish the storage of zinc in the human body, thus militating against the theory that zinc is harmless because it is not stored.

Mallory [13] has recently reported the causing of nephritis in animals due to the action of metallic zinc implanted subcutaneously. Schwartze and Alsberg [14] investigated zinc sulphate as an emetic. In the course of this work intravenous injections of zinc sulphate brought about a gastric and intestinal inflammation. Salant [15] after feeding rats weighing from 150 to 200 g., 10 to 15 mg. of zinc acetate daily for 4 months, observed no impairments, with the possible exception of renal disturbance. Sacher [16] reported that zinc-fed rabbits developed albuminuria, renal congestion, gastric petechial hemorrhage. Brandl and Scherpe [17] fed zinc to animals and observed on autopsy, hemorrhage into the gastric mucosa, renal congestion and cloudy swelling. Salant and Wise [18] introduced small quantities of zinc (10 mg. per kg. of animal weight) directly into the circulation and noted marked injury to the kidneys, nephritis, glycosuria, leading to death in a few days.

Wherry [19] injected intravenously zinc acetate in dilutions of 1/20,000 of rabbit body weight. No manifestations developed in this experiment until the third day when the animal was found dead. A dilution of 1/32,000 per body weight was non-fatal. A higher concentration than 1/20,000 caused immediate death, or death within a short time. In the one case where death followed 1/20,000 dilution, there was observed on post-mortem marked edema of the lungs, a sero-hemorrhagic exudate into the peritoneal cavity, marked nephritis, swollen, gray kidneys with petechial hemorrhage. The stomach was not examined.

Application of zinc as treatment for cancer, particularly of the uterus, has led to absorption and systemic poisoning.

A skin disease attributed to zinc oxide powders has been found among workers in that chemical, by Turner.[20] McCord and Kilker [21] have described ulcers on the extremities of workers in a wood preservation plant wherein zinc chloride was used as a fungicide.

Witthaus [22] enumerates 59 deaths from the effects of zinc chloride, and 29 from zinc sulphate. In all of these the zinc salt was taken in error, or for suicidal or homicidal purposes. Both the immediate and late results center about the corrosive or irritant action on the intestinal tract. The lethal dose is not known because of the emetic action of these salts leading regularly to loss of at least part of the substance. The smallest known quantity of the sulphate causing death was 15.5 g.

Blyth [23] records the developments in a patient who died 14 weeks after taking a tablespoonful of "Burnett's fluid," an aqueous solution of zinc chloride.

In discussing sulphate of zinc, Blyth states, "The infrequency of fatal results is due not to any inactivity of the salt but rather to its almost always being expelled by vomiting."

This review of the toxicology of zinc is not offered as a complete one. Sufficient is here included to convince that this metal has a greater toxicity than is commonly recognized by either zinc industrialists or physicians.

SUMMARY

In a small galvanizing plant, we have detected widespread gastrointestinal conditions, varying from gastroenteritis, in the younger workers, to well-established gastric and duodenal ulcers among workers employed for a long time. Twelve out of 15 workers employed 6 years or longer have presented severe gastrointestinal lesions.

In a second plant, wherein all employes are new at this work (less than 6 years) and wherein the general work conditions are better and exposure to trade process fumes is much less, no cases of this gastrointestinal disease have been found.

We have shown the accidental formation of zinc sulphate and zinc chloride at levels and under conditions that involve exposure on the part of workers in Plant 1.

In workers whose urine has been tested, zinc has been found in quantities in excess of accidental urine content from food, galvanized iron pipes, etc.

These patients have not presented the characteristics of other occupational disease hazards attending galvanizing.

We have sought to stress the occurrence of multiple hazards in the galvanizing industry. On this account we feel unwarranted in drawing any precise conclusions as to the etiologic factor in these cases. Although we attach significance to zinc as a causative agent, we accept various other substances as possible contributing factors. We also believe that the unhygienic condition of the work place, together with the physical type of worker, favor the occurrence of the conditions described.

A close resemblance is seen between our observations of lesions among zinc workers and the findings in the literature referred to wherein study has followed the administration of single, chemically pure substances. Our concept that zinc is capable of producing chronic systemic poisoning is aided (a) by the work of Mallory in obtaining kidney lesions from pure metallic zinc implanted subcuta-

neously, thus disproving the oft-repeated statement that metallic zinc is non-poisonous; (b) by the work of several authors establishing stored zinc in appreciable quantities in various organs and tissues and in excreta of zinc workers, long after the discontinuance of zinc work; (c) by the creation of alimentary tract lesions by pure zinc salts administered intravenously and by mouth.

A long period of time expressed in years (5 to 20) appears necessary for the production of the lesions described.

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Connecticut Public Health Association—The Connecticut Public Health Association held its second meeting for the season at the Welfare Building at Bridgeport, Connecticut, on February 11 with Professor Winslow in the chair. At the morning session Dr. W. H. Coon discussed scarlet fever as an atypical disease, and Professor F. B. Blake of the Yale School of Medicine gave an address on scarlet fever in which he described in detail the prevalence of the disease in its toxemic and septic phases, and described exactly what may or may not be expected from the scarlet fever serum in treatment and prevention.

After a luncheon at which the Association was entertained by Dr. Coon and his associates of the Bridgeport Health Department, Dr. Haven Emerson of Columbia University spoke on the preventable diseases of adult life, and on the basis of a detailed statistical analysis demonstrated the diversity of the behavior of these diseases and the importance of studying each one as an entity by itself, pointing out that the generic term "degenerative disease" is as misleading as the term "zymotic diseases" of the past.

New Rules for the Painting Trades—Announcement is made by the Massachusetts State Department of Labor and Industries that new rules for those in the painting business have been adopted and became effective Jan. 1, 1926. These regulations concern general safety provisions; requirement for registration; general health requirements especially intended to provide protection for workmen using spray coating apparatus. Operators of such apparatus shall be provided with respirators or other effective devices, and exposed parts of the body shall be anointed with a harmless non-drying oil, grease or cream. Dr. Wade Wright served as chairman of the special committee which assisted the Massachusetts Department of Labor and Industries in preparing the new rules.—Mass. Dept. of Labor and Industries, Boston, Mass.